

IV.E.5 The Reactivity Properties of Hydrogen Storage Materials in the Context of Systems

Daniel Dedrick (Primary Contact),
Richard Behrens, Michael Kanouff,
Robert Bradshaw, Joseph Cordaro, Joseph Pratt,
Craig Reeder

Sandia National Laboratories
PO Box 969 MS 9409
Livermore, CA 94551-0969
Phone: (925) 294-1552
E-mail: dededri@sandia.gov

DOE Technology Development Manager:
Ned Stetson

Phone: (202) 586-9995
E-mail: Ned.Stetson@ee.doe.gov

Project Start Date: July 5, 2007
Project End Date: September 30, 2010

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Objectives

- Develop generalized methods and procedures required to quantify the effects of hydrogen storage material contamination in a systems environment:
 - Quantify chemical processes and hazards associated with high- and low-level contamination of hydrogen storage materials.
 - Predict processes during accident scenarios of systems containing hydrogen storage materials.
 - Identify and demonstrate ex situ and in situ hazard mitigation strategies.
- Provide technical basis for codes and standards efforts when appropriate technology maturity has been attained to enable the design, handling and operation of effective hydrogen storage systems for consumer and industrial applications.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

- (D) Durability/Operability
- (F) Codes and Standards
- (Q) Reproducibility of Performance
- (K) System Life-Cycle Assessments

Technical Targets

Technical targets addressed mainly focus on environmental health and safety. This project is enabling the satisfaction of these targets by providing the technical basis for future codes and standards efforts, thus enabling the design, handling and operation of effective hydrogen storage systems.

Environmental Health and Safety

Toxicity	Meets or exceeds applicable standards
Safety	Meets or exceeds applicable standards

In addition to the above target, other storage technical targets are impacted by this effort as follows:

- Gravimetric and Volumetric Capacity - This parameter may be influenced by added weight and volume of developed safety systems and mitigation strategies; for example, contamination permeation barriers etc.).
- Storage System Cost - System cost may be impacted by engineering controls that are developed.
- Fuel Purity - Current draft fuel purity standards are based on proton exchange membrane fuel cell requirements. Hydrogen storage materials may have more stringent hydrogen purity requirements.

Accomplishments

- We have found that the hazard presented by the breach-in-tank scenario is significantly minimized when loss of hydrogen was considered.
- We have determined that over-pressures and over-temperatures are probable during a pool fire scenario involving an un-mitigated metal hydride bed.
- We have polymerized both catalyzed and un-catalyzed complex metal hydrides, sodium alanates with vinyl monomers at 10 and 20 wt% (mitigated samples produced).
- We have demonstrated that mitigated samples show a nearly a 70% reduction in energy released during oxidation.

- We have successfully hydrogen cycled polymerized and mitigated samples nearly 160 times.
- We have quantified the impact of cross-linking density on the structural properties of mitigated materials.
- We have scaled up synthesis of mitigated materials to 10 g to enable larger scale testing and analysis.



Introduction

This project is focused on developing generalized methods and procedures required to quantify the reactivity properties of hydrogen storage materials to enable the design, handling and operation of solid-state hydrogen storage systems for consumer and industrial applications. We are performing the experimental and theoretical efforts that are required to understand processes during high-level contamination events including accidents, and low-level contamination events experienced during the life cycle of the storage system. This effort provides the technical basis of the identification of hazard mitigation strategies, and eventually development of appropriate codes and standards. A successful effort in quantifying the reactivity properties of hydrogen storage materials will enable the safe design, production, handling, operation, and disposal of consumer and industrial hydrogen storage systems and provide the technical basis for eventual standards developed for safe hydrogen storage systems.

Approach

We take a science-based approach to understanding, predicting, and controlling contamination processes of hydrogen storage materials. By first understanding the fundamental contamination reaction processes using combination of established and newly developed experimental techniques, we are able to build robust and useful chemical kinetic models. These chemical kinetic models are then coupled with heat and mass transfer characteristics to assemble validated models of contamination scenarios. These validated models are then exercised to develop an understanding of the engineering and administrative controls required to mitigate the hazards caused by the contamination processes in the context of systems.

Results

Prediction of processes during accident scenarios and the development of mitigation technologies for solid state hydrogen storage systems were the focus of efforts in Fiscal Year (FY) 2010.

Efforts to predict processes during accident scenarios investigated the impact of hydrogen evolution on the breach-in-tank contamination scenario, and the fire impingement scenario. In brief, we have determined that the evolution of hydrogen from the bed reduces the extent of the oxidation reaction during a breach-in-tank scenario. We have also determined that a pool fire scenario can lead to a system over-temperature and over-pressure event within a short time of exposure. As a result of this analysis we have identified to mitigation strategies for further development (1) additives that limit the extent and rate of oxidation and, (2) thermal shielding design to limit the reduce the rate of temperature rise within the system during a fire.

Breach-In-Tank Scenario Modeling – We have considered the case in which an accident results in air exposure of alane contained within a tank. We have built our models using desorption kinetics of alane combined with our model parameters developed for permeability and oxidation kinetics. We considered the realistic case for the alane bed breach-in-tank where heat losses to the environment at $5 \text{ W/m}^2\text{-K}$ cool the bed after the initiating event. Considering a one inch diameter, one foot long cylinder (characteristic geometry utilized in the simulations) filled with alane at 0.33 g/cc , calculations indicate that the oxidation reaction is significantly inhibited by the evolution of hydrogen. The loss of hydrogen from the system initially cools the bed to $\sim 85^\circ\text{C}$ prior to any inclusion of air into the bed (Figure 1). These results indicate that an alane breach-in-tank event may present a minimal hazard during an accident. Of course, this analysis is specific to this formulation of alane and the characteristic tank geometry.

Other materials may be much more reactive compared to the alane system. Catalyzed sodium alanates, for example, are materials that represent a prototypical alkali-metal containing complex metal hydride. Our experimental measurements utilizing our contamination flow-through reactor show that catalyzed sodium alanates and their decomposition products are significantly more reactive. Exotherms in excess of 100°C are sustained for nearly 250 s upon exposing a 300 mg sample of hydrogen-depleted material to dry air. Analysis of the products indicates the formation of sodium hydroxide (NaOH) at these temperatures. Mitigation technologies to reduce the extent and rate of reaction during the breach-in-tank scenario are considered below.

Fire Impingement Scenario Modeling - Exposure to a pool fire is one of the potential scenarios associated with solid-state hydride storage systems that might result from a vehicle accident.

The sodium alanate containing system provides an opportunity to observe the processes of a complex hydride during exposure to a pool or impinging fire. For

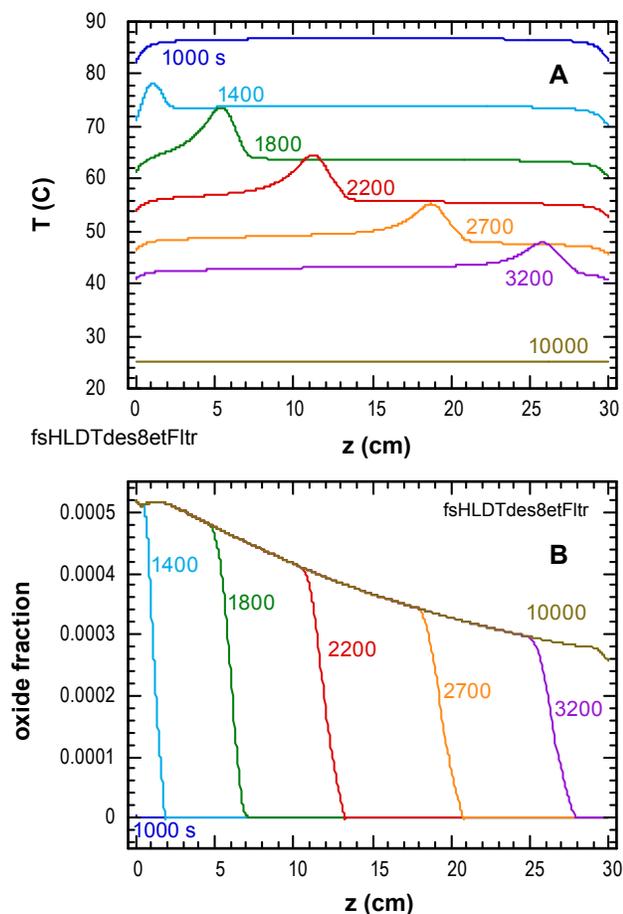


FIGURE 1. Breach-in-tank scenario for a desorbing alane bed. A moderate reaction front proceeds for nearly 1 hour (A) with only a small fraction of the alane oxidized (B).

this system, it is assumed that the formation of sodium metal due to overheating is the outcome requiring management. Using measured heat transfer, mass transfer, and chemical kinetics, an axisymmetric model was assembled for analysis (Figure 2). The results show that a thin desorption front develops in the sodium alane starting at the outer tube wall, which is heated directly by the fire, and then propagates radially inward. The calculations account for the rapid desorption of the sodium alane resulting from the fire. Assuming that sodium metal would begin to form at near 350°C, the unshielded case achieves this temperature very quickly, after 180 s. A small amount of shielding (a thin air gap formed by a metal plate) extends this over-temperature event to 300 s – providing good management of the over-temperature hazard. Similar analysis can be performed for a variety to materials, such as alane or interstitial hydrides, to manage the resulting over-temperature or over-pressure hazard. The pool fire scenario may be one of the more important safety design considerations for metal hydride containing systems. This effort scopes details such as pressure relief device

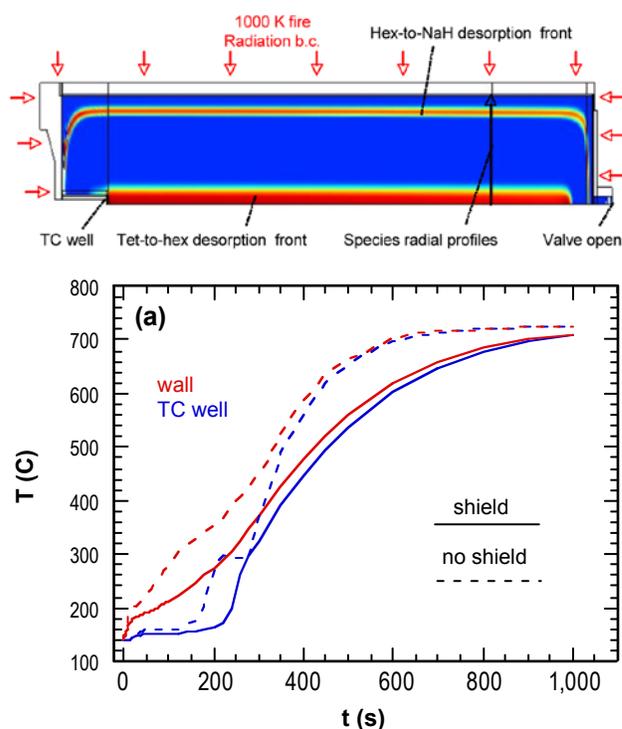


FIGURE 2. Axisymmetric model assembled for analysis of the fire impingement scenario involving a sodium alane containing system. Results indicate that the over-temperature condition can be delayed with the use of simple thermal shielding.

and insulation design characteristics required to allow for an adequate delay in loss-of-containment during an accident scenario.

Mitigation Technology Development – Towards the goal of mitigating and managing the hazards presented by solid state storage systems, we have demonstrated the ability to polymerize vinyl monomers in the presence of complex metal hydrides, sodium alanates and produce composite materials.

Composite materials were made with 10–20 wt% polymer. Characterization of the composite polymer/metal hydride material was done by scanning electron microscopy and thermal methods. Figure 1 and the accompanying energy dispersive spectrum (EDS) analyses show that the polymer is intimately mixed with the metal hydride particle. The inorganic portion was identified by the strong Na, Al and O signals in the accompanying EDS. The polymer surrounding the inorganic material was identified by the absence of Na and Al signals and the shoulder at low energy for carbon, C. Thermal analysis of composite materials compared to free sodium alane suggests slower kinetics for mass-transport properties of the melted metal hydride above 150°C.

To test the mitigating properties of the polymer supported material, 360 mg of the polymerized material were analyzed using flow-through calorimetry. The

exotherm resulting from dry gas exposure at 200°C and 0.1 SLPM air was compared to the un-mitigated “neat” material results (Figure 3). It was observed that the energy release was reduced by nearly 70%, indicating that a significant portion of the sample was excluded from oxidation. This was confirmed by product analysis indicating very little formation of NaOH in the mitigated sample compared to the un-mitigated sample. In parallel, catalyzed and supported samples of sodium alanate were hydrogen cycled. Initial results indicate that hydrogen uptake/release is not significantly hindered and even at high cycles (in excess of 30 hydrogen sorption cycles executed). The cycled material was then analyzed by thermal gravimetric analysis (TGA). Results show that the cycled material has an 11% weight loss upon heating, similar to the uncycled material. Our conclusion from this study is that the polymer matrix withstands at least 30 cycles of charging with no indication in loss of polymer matrix.

To optimize the structural properties of the material, the cross-linking density of the added polymer has been varied to determine the effect on mechanical properties. Monomer/cross-linker ratios of 10:1 to 1:1 have been explored. Our results show that with higher cross-linker ratios, the composite materials are more brittle and are easily crushed into a powder. In contrast, the composite materials with a lower cross-linker ratio (10:1 monomer/cross-linker) give very hard solids that are not easily crushed into powders. Little change in decomposition behavior is observed despite large structural properties changes. TGA of the composite materials in argon shows polymer decomposition occurring above 220°C with approximately 11–12 wt% loss (Figure 4). This mass loss is expected since significant char formation

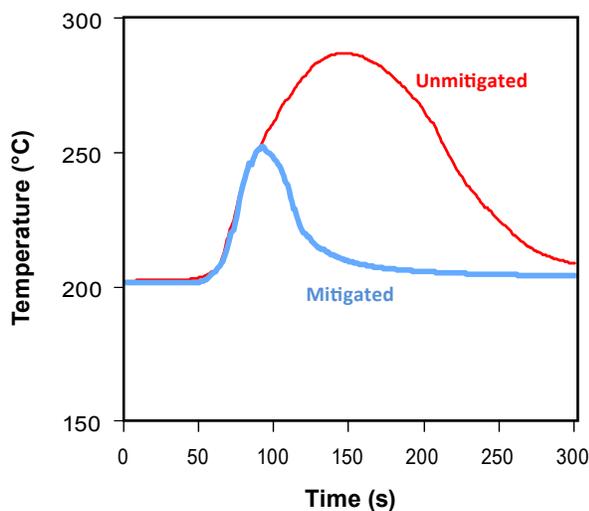


FIGURE 3. A comparison is shown for materials with and without mitigation polymer. It can be observed that the energy released is reduced by nearly 70%, indicating significant progress in mitigation technology development.

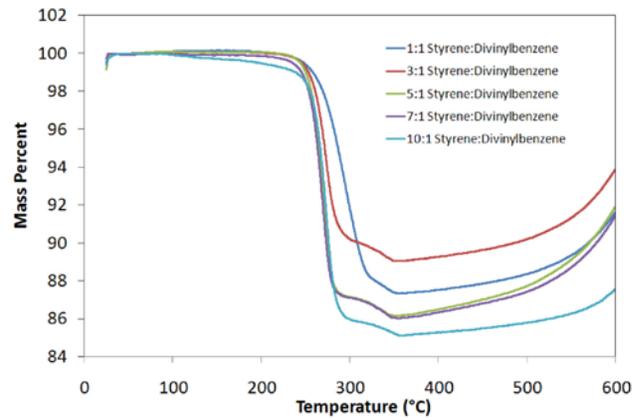


FIGURE 4. TGA comparison of various cross-linking densities indicates little change in decomposition behavior in spite of large structural properties changes.

occurs in cross-linked polymer networks upon thermal decomposition.

Conclusions and Future Directions

- This project has developed the tools and understanding for eventual codes and standards development and market penetration of metal hydride systems.
- Over-temperature and over-pressure events caused by exposure to air or fire are hazards that need to be managed to enable the widespread utilization of advance hydrogen storage materials.
- Mitigation technologies are being developed that are able to:
 - Contribute a small weight penalty
 - Withstand hydrogen cycling
 - Mitigate unfavorable reactions
 - Structurally support fine reactive solids
- Future work will focus on:
 - Optimization of composite materials
 - Validation at full-scale
 - Enabling design-for-safety of advanced storage systems

Special Recognitions & Awards/Patents Issued

1. IEA HIA 2010 Project award for technical excellence presented at WHEC 2010.

FY 2010 Publications/Presentations

1. D. Dedrick, J. Cordaro, M. Kanouff, R. Bradshaw and Y. Khalil “Mitigating hazards during accident scenarios involving metal hydride materials”, *Proceedings from NHA 2010, Long Beach, CA, May 3–6, 2010.*

2. D. Dedrick, M. Kanouff, J. Keller, T. Voskuilen, “*Optimization of hydrogen uptake and release in automotive-scale metal hydride systems*”, Proceedings from WHEC 2010, Essen, Germany, May 16–19th, 2010.
3. D. Dedrick, M. Kanouff, R. Larson, R. Bradshaw, J. Graetz, S. Hwang. “*Predictions of solid-state hydrogen storage system contamination processes*”, Proceedings from the ICHS 2009, Corsica, Fr. Sept 16–18th, 2009.
4. N. Rubin, J. Cordaro, D. Dedrick, “*Thermal Stability of Organic Microporous Polymers Packed with Hydrogen Storage Materials*”, 2008 - Polymer Degradation Discussion Group, Sestri Levante, Italy, 6th & 10th Sept, 2009.
5. D. Dedrick (presented by M. Alendorf), “*Reactivity of solid state hydrogen storage materials*”, IEA Task 22 Experts Meeting, Paris, France, October 10, 2010.